

ATYPICAL LOCAL ACCUMULATION OF CALCIUM CARBONATE DEPOSITS IN PREHISTORIC CERAMICS DURING UNDERGROUND LYING

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Abstract. *The study focused on an anthropomorphic female statuette from a ritual complex discovered in the LI dwelling from the Precucutenian settlement of Isaiia, Iași County (Romania). Statuette no. 6 was broken in two along a line running across the pelvis, and the resulting sectional profile is bilobed. The interior of the pelvis presented macroporous grezous cavities filled with crystallized calcium carbonate, of immaculate white colour and hardness greater than that of gypsum. The investigation (SEM-EDX and micro-FTIR) revealed the presence of aragonite (an allotropic form of calcium carbonate) originating from active calcium carbonate (calcite) that matured and coalesced as the aluminosilicate structures dissolved. The deposit presents a peculiar arrangement resulting from an atypical sequential process of chronological concentration through ion exchange chemical reactions, and through processes of direct osmosis via the semi-membrane system of the slip clogged with phosphate, silicate, and aluminate anions during lying in the presence of chlorine, phosphate and sulphate anions, as well as potassium, magnesium and iron cations from the soil. The experimental data explain the chemical processes behind the formation of this mineral deposit, stable and sparingly soluble, resulting from natural rather than anthropic causes.*

Keywords: Chalcolithic, Precucuteni culture, aragonite, anthropomorphic female statuette, SEM-EDX, micro-FTIR.

1. Introduction

It happened many times that an archaeologist would find in the breaks or cracks of some prehistorical ceramic item (especially in anthropomorphic statuettes), localised deposits of a monolithic white substance, with a hardness greater than that of gypsum, beautifully crystallised at the nanostructural level. Not knowing the chemistry behind the manufacturing process (Goffer 2007) archaeologists believed these substances present in the paste of the ceramic had anthropic origins, ascribing to them a cultic character.

This interpretation would seem to have been not far from the truth if we consider the fact that in the paste of several Precucuteni (Trypillia A) and Cucuteni (Trypillia B) anthropomorphic female statuettes archaeologists have identified impressions of cereal caryopses, either whole or crushed, which were confirmed through X-ray radiography (Monah 1997, 52–53). Moreover, the paste of a statuette belonging to the Linear Pottery culture displayed traces of cereal flour (Höckmann 1987, 90–91, fig. 1/1–2). This deliberate mix has been interpreted as a ritual gesture through which the body of the goddess (the statuette), standing in for *Terra Mater*, was inseminated (Monah 1997, 54).

The recent attempt to preserve and the well-known cultic complex from Isaiia, Iași County, Romania (Ursulescu and Tencariu 2006), belonging to the 2nd phase of the Precucuteni culture (Figure 1), lead to the identification in the transversal break along the pelvis of the anthropomorphic statuette no. 6

(Figure 2), of a white-coloured deposit in the central area of the two buttocks (Figure 3). Even if it was obvious that any organic material in the paste would have not been preserved to this day, we nonetheless pursued the question of what is the cause of this deposit, by subjecting it to a co-joint SEM-EDX–micro-FTIR analysis.

2. Experimental part

To investigate the deposit of crystallised and aggregated salts we employed two modern methods based on the system of technique co-assistance, SEM-EDX and micro-FTIR.

We used a scanning electron microscope, SEM VEGA II LSH model, produced by TESCAN, coupled with an EDX detector QX2 QUANTAX type, manufactured by Bruker/ROENTEC Germany. The microscope, fully controlled via computer, has an electron gun with a tungsten filament that can achieve a resolution of 3nm to 30kVA, with a magnification of 30×, a 1.000.000× operating mode "resolution" of acceleration voltage between 200V to 30kV, and a scanning speed of 200ns and 10ms per pixel. The pressure is less than 1×10^{-2} Pa. The resulting image can be formed by secondary electrons (SE) and backscatter electron (BSE).

The Quantax QX2 EDX detector was used for qualitative and quantitative micro-analysis. The EDX detector is of the third generation (X-Flash), which does not require liquid nitrogen cooling and is about 10 times faster than conventional Si (Li) detectors.

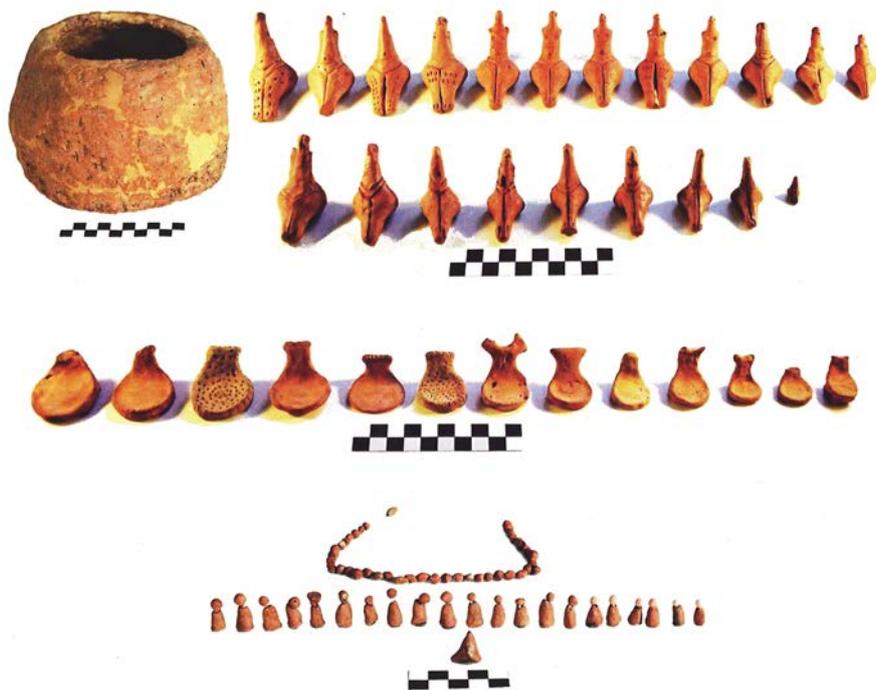


Figure 1. The cultic complex from Isaiia, Iași County, Romania; phase II of the Precucuteni culture (apud Ursulescu and Tencariu 2006, pl. III).

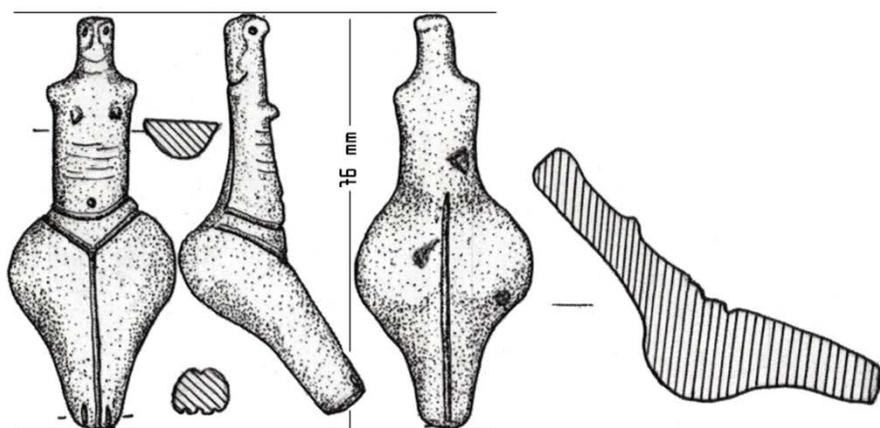


Figure 2. Statuette no. 6. Drawing (ap. Ursulescu and Tencariu 2006, fig.22/6).



Figure 3. The broken statuette no. 6 with white mineral deposits in the central area of the buttocks.

The analysis technique, alongside the inspection of the microphotograph, allows the rendering of the image with the map (layout) of the atoms on the investigated surface. On the basis of the X-ray spectrum, we can also establish the elemental composition (in gravimetric or molar percentages) of a microstructure or of a selected area, and also to assess the compositional variation along a vector running along the surface or section of the investigated structure.

2.2. The micro-FTIR Analysis

The spectra were recorded using a FT-IR spectrometer coupled by a HYPERION 1000 microscope, both manufactured by Bruker Optic.

The FT-IR spectrophotometer is a TENSOR 27 type, which is adequate particularly for measuring in the Near-IR spectrum. The standard detector is a DLaTGS that covers the spectral domain between 7500 and 350cm⁻¹. The TENSOR 27 is equipped with a He-NE laser that emits at 633 nm and at a power of 1mW, and with a ROCKSOLID alignment of the interferometer. The signal-to-noise ratio is very high. The device is fully controllable through the dedicated OPUS software package.

The HYPERION 1000 microscope is an accessory that can be coupled with almost any Bruker FT-IR spectrometer. For measurements that are completely non-destructive, the TENSOR 27 spectrophotometer is coupled to the HYPERION 1000 microscope; the

solid samples are generally handled in reflection mode.

The OPUS/VIDEO software allows for interactive video data acquisition, in two working configurations (in transmission and in reflexion). The detector is a MCT type, cooled with liquid nitrogen (-196°C).

The spectral domain is $600\text{--}7500\text{cm}^{-1}$, and the measured area is optimised at a diameter of $250\mu\text{m}$, with the possibility of reaching a minimum of $20\mu\text{m}$. The microscope is equipped with a $15\times$ lens.

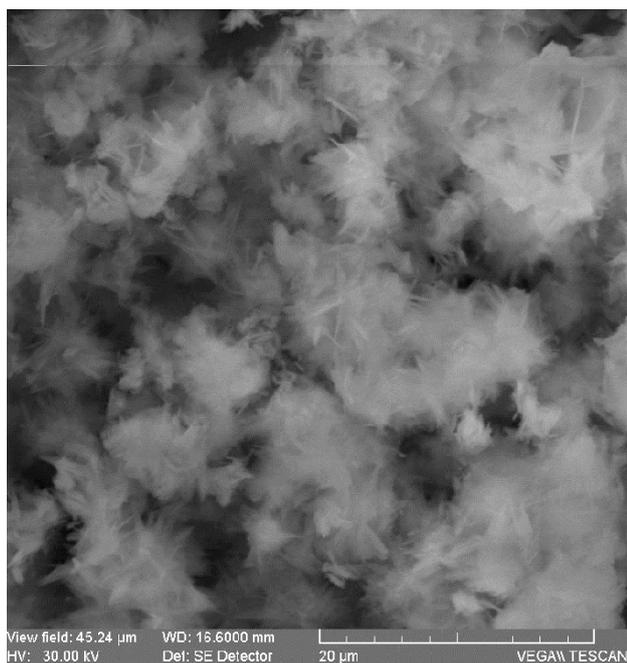


Figure 4. The SEM microphotography of the aragonite acicular crystallites from the central area of the deposit.

3. Results and discussion

Figure 4 depicts the microphotography of the crystallites at $5000\times$ magnification, collected from the central area of the deposit, in the central portion of the cavities formed during lying inside the buttocks, in which the presence of acicular nanostructures clustering together in immaculately-white, puffy clumps is clearly visible.

The EDX spectrum (Figure 5), on the basis of which the gravimetric and atomic percentage composition was assessed (Figure 1), clearly shows that the deposit is composed of calcium carbonate (in the aragonite allotropic form), which accumulated during underground lying under the influence of pedological factors. The lying stratigraphic level is characterised by a chemical loading that varied throughout time in terms of concentration, pH, and

temperature. Because of these conditions, the crystallisation and aggregation occurred in several stages, during a long time span, apparently simultaneously with the processes that lead to the formation of the cavities through the dissolution and segregation of the aluminosilicates. Such stable deposits form through an acidic-basic mechanism of ion exchange in which Ca^{2+} ions in the lying environment react in slightly alkaline mediums generated *in situ*, with HCO_3^- hydrous carbonate anions. The acicular (puffy) nanostructures, which are very rigid at the macro level, bear witness to a long crystallisation and maturation-aggregation period.

The directed concentration of aragonite is explained by the osmotic potential generated by the difference in concentration, with two processes taking place concurrently and in opposite directions: (1) the penetration through diffusion and osmosis of the two reactant species (Ca^{2+} and HCO_3^-) from the surface towards the two cavities inside the buttocks, and (2) the formation of the two cavities through the dissolution and segregation of the ceramic structures. The propensity for dissolution of these internal structures is due to the difference in porosity and hardness between the surface and the core of the artefact during the manufacturing stage, and the diffusion of the reactant species from the lying environment towards the internal structures is due to the osmotic pressure generated by the engobe, which acts as a semi-permeable and selective membrane.

The EDX spectrum in Figure 8, created on the basis of the microstratigraphic structures in Figure 7, reveals a series of ionic components (Figure 9) that originated from the lying environment and the solubilisation of the artefact's central internal ceramic structures.

The forming of the nanostructured aragonite deposit was due to specific conditions created by the fine, microporous ceramic from the core of the statuette's buttocks, and the presence of HO^- and Ca^{2+} ions and of several other ionic species with alkaline reactivity (K^+ , Mg^{2+} , Fe^{2+} , HPO_4^{2-} , etc.), with the aluminosilicate crystallites (acting as crystallisation stems for the calcite) suffering from processes of dissolution and segregation towards the surface of the artefact. Their role as crystallisation agents favoured, following the dissolution processes, the conversion of the calcium carbonate structure, from calcite to aragonite. In these conditions, the Ca^{2+} ions, in the presence of the alkaline precursors, interacts with

the hydrous carbonate anion, which then converts, through decomposition, first to calcite. The substitution of the aluminosilicate crystallisation stems with calcium carbonate drives the densification of the calcite, which then, through maturation, converts to aciculary crystallised aragonite. During the lying period, the osmotic processes for the Ca^{2+} and HCO_3^- ions directed from the surface of the ceramic item towards the deposit in the cavities, concurrently with the solubilised silicate and aluminate ions going from the core to the surface of the artefact, lead to a gradual maturation of the crystallites, followed by the monolithisation of the aragonite.

When the statuette was discovered, the deposit inside was well consolidated, with a hardness between that of gypsum and of fluorite.

Figure 10 presents the FTIR spectre, which confirms the chemical nature of the aragonite deposit, unpurified by precursors and aluminosilicates from the ceramic, as attested by the representative peaks of the specific group vibrations for the species carbonate (697cm^{-1} , 730cm^{-1} , 1306cm^{-1}), silicates (620cm^{-1} and 1162cm^{-1}), aluminates (813cm^{-1}), water from crystal hydrates (1617cm^{-1}), and those physically bound by hydrogen, aqua-, and hydro-complexes bonds (3403cm^{-1}).

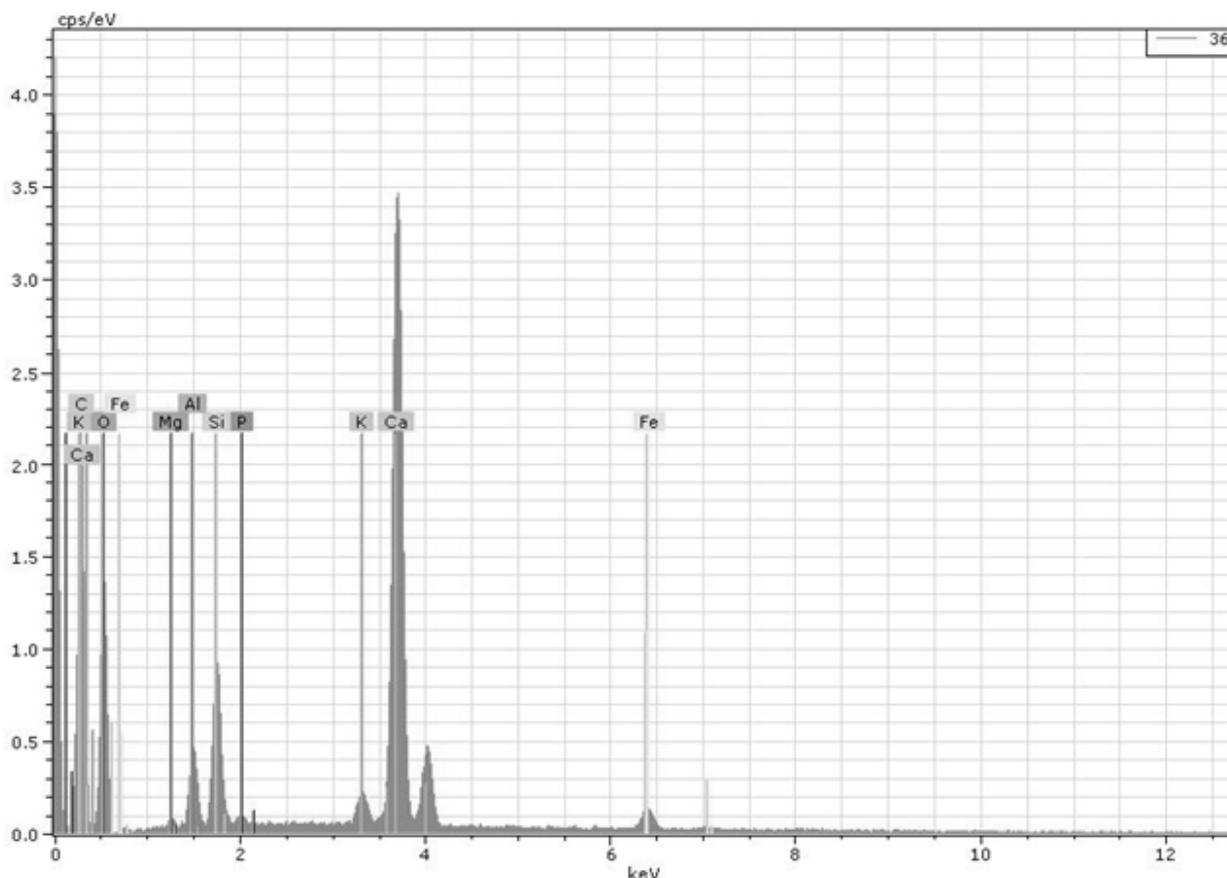


Figure 5. The EDX spectrum of a sample collected from the core of the deposit.

Element	[norm. wt.-%]	[norm. at.-%]	Error in %
Calcium	17.38394	7.904066	0.656452
Carbon	6.072849	9.213439	2.441248
Silicon	4.044039	2.623865	0.253939
Aluminium	2.021104	1.364993	0.159749
Iron	0.915657	0.298773	0.064532
Potassium	0.758237	0.353391	0.05959
Magnesium	0.316153	0.237034	0.058058
Oxygen	68.48802	78.00444	11.00388
-	100	100	-

Figure 6. The elemental composition of the deposit in gravimetric and molar percentages.

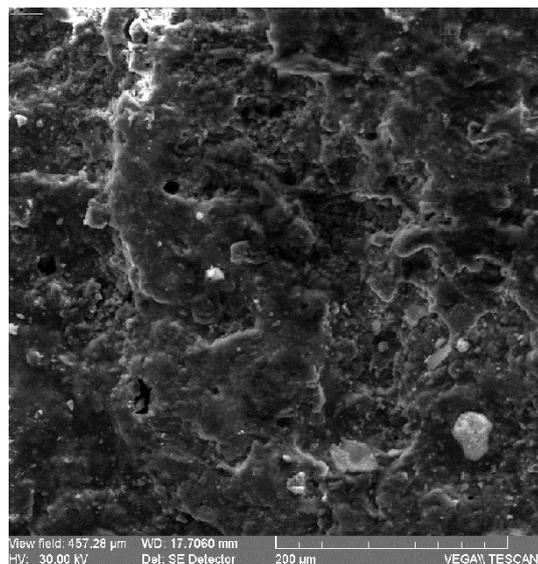


Figure 7. The SEM microphotograph of the structure inside the statuette.

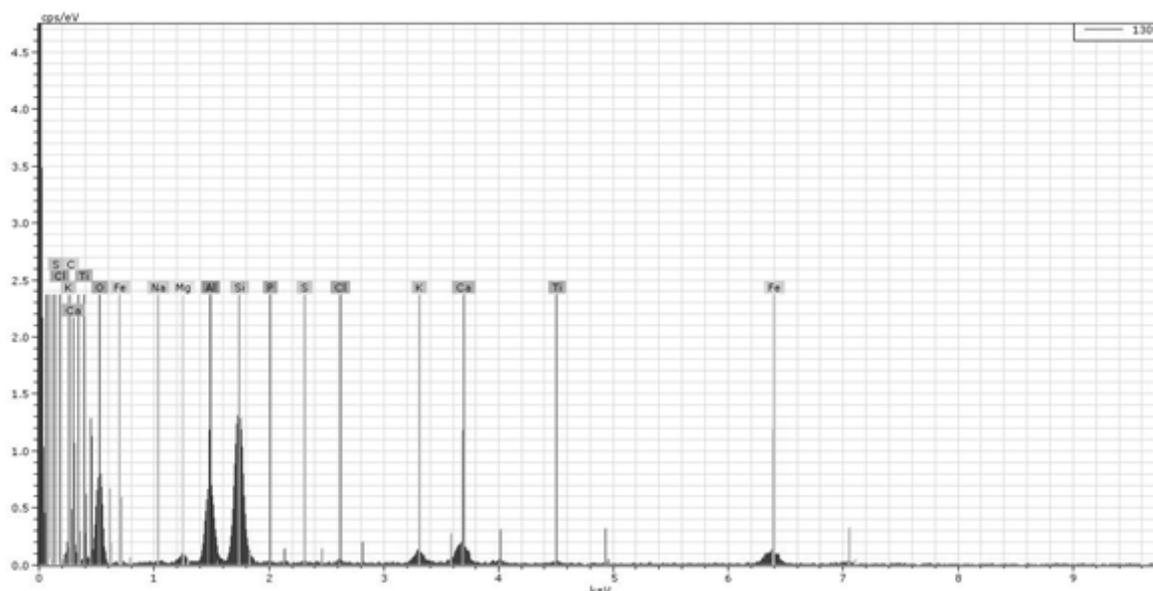


Figure 8. The EDX spectrum for the mineral structure inside the statuette.

Element	[norm. wt.-%]	[norm. at.-%]	Error in %
Silicon	22.28747	15.92341	1.039876
Aluminium	11.60182	8.628138	0.633296
Iron	4.128861	1.483501	0.161587
Titanium	0.52068	0.21821	0.057164
Calcium	3.761646	1.883343	0.159733
Carbon	6.22557	10.40058	2.681186
Phosphorus	0.306343	0.198459	0.054398
Magnesium	1.648245	1.360767	0.151271
Potassium	1.931946	0.991505	0.105144
Sodium	1.114372	0.972643	0.142394
Chlorine	0.313876	0.17765	0.049965
Sulphur	0.205783	0.128772	0.045435
Oxygen	45.95339	57.63302	44.70424
-	100	100	-

Figure 9. The elemental composition of the statuette's internal structure.

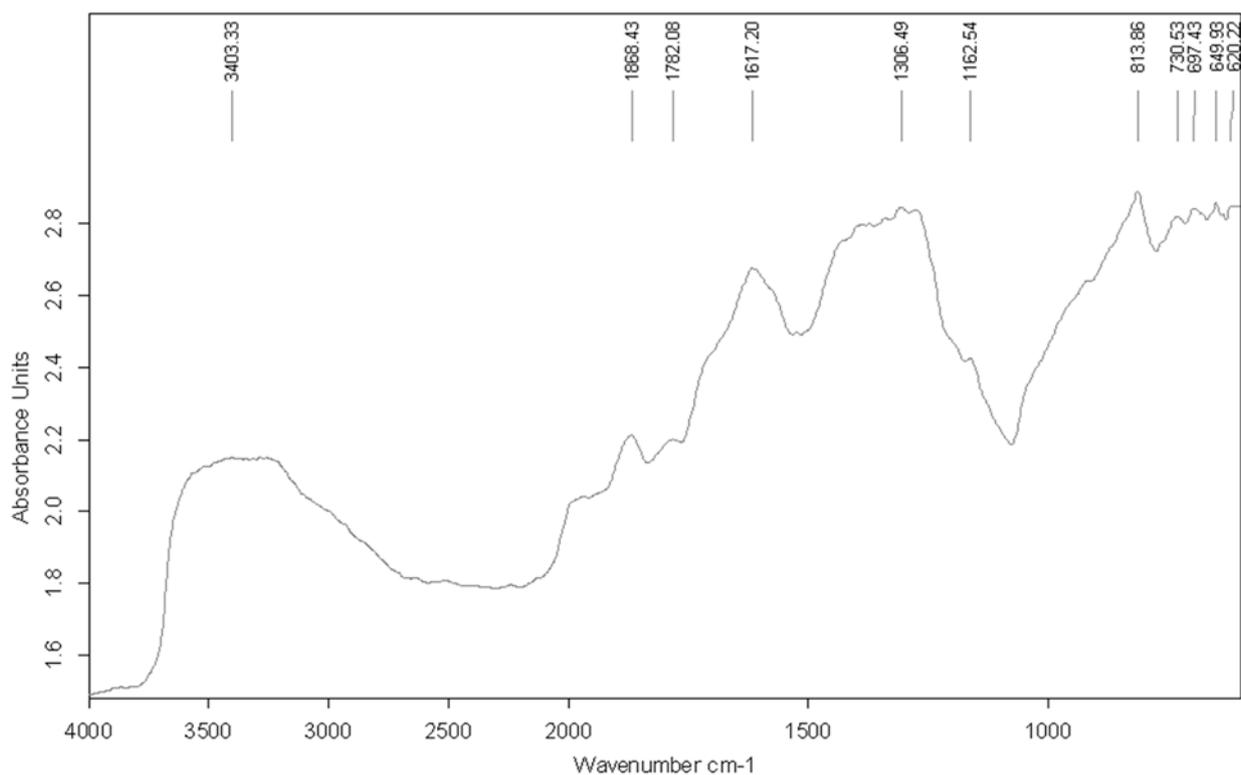


Figure 10. The FTIR spectrum of the aragonite deposit.

4. Conclusions

The data provided by the SEM-EDX and micro-FTIR experimental investigation revealed that the mineral deposit from the cavities within the buttocks of a female anthropomorphic Precucuteni statuette is aragonite. The deposit has an immaculate-white colour, and was formed during the time the artefact lay buried, when two simultaneous processes took place in opposite directions: (1) the diffusion and osmosis from the surface towards the two internal cavities of the Ca^{2+} , HCO_3^- , and HPO_4^{2-} ions; and (2) the dissolution and segregation of the ceramic aluminosilicate structures from within the buttocks, and the formation of the two cavities.

The high solubility of these internal structures was an effect of the difference in porosity and hardness between the surface and the core of the item, features which are the direct results of the manufacturing technique employed by the craftsman; similarly, the difference in the osmotic pressure was due to the engobe, which acted as a membrane at the surface of the statuette.

The monolithic aragonite deposit formed through the aggregation of active calcium carbonate is attributable to the processes of densification and maturation involving aluminosilicate crystallisation stems that were gradually solubilised and replaced with carbonate anions. Therefore, during lying, the

two concurrent osmotic processes caused the maturation of the calcite crystallites, followed by the monolithisation of the aragonite; when the statuette was discovered, the deposit was well cemented, and possessed a hardness between that of gypsum and of fluorite.

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